Vacuum Pyrolysis of Bituminous Coal

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ABSTRACT

An apparatus is described for the vacuum pyrolysis of bituminous coal. Attention is focused on the solid red-brown lacquer which is distilled on to a condensing surface located just above the coal sample. Infrared and ultraviolet spectra, molecular weight, molar refraction, solubility data, and softening temperatures are reported. Two experimental techniques are presented: (1) molecular weight determination by means of boiling point elevation of a binary azeotropic mixture, and (2) preparation of solid samples for spectral analysis by vapor condensation on polished NaCl and KBr plates. It is concluded that the solid condensates represent primary decomposition products which have a close resemblance to the parent coal.

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Thermal degradation of coal yields gaseous, liquid, and solid products. The pri mary decomposition products which are initially formed probably decompose in turn, ar the resulting fragments react further with each other and with the solid residue to form the observed tars, liquors, gases, and char. Due to these secondary reactions the decomposition products which are eventually observed may be far removed from the original coal structure, offering few clues to the chemical constitution of coal.

Pyrolysis of coal under reduced pressures has been used to minimize these secon dary reactions. The history of vacuum pyrolysis of coal is reviewed by Howard (1), who reasoned that all of the early investigations suffered from secondary reactions because of poor vacuums (hence slow removal of the primary decomposition products from the heated zone), and long distillation paths (causing the primary decompositio products to suffer numerous molecular collisions in the gas phase, or collisions wit heated surfaces near the sample holder). Locating the condenser within a distance o one mean free path of the sample holder would allow the primary decomposition produc to be collected before secondary reactions took place. In line with these considera tions, Juettner and Howard (2) constructed a molecular still for the pyrolysis of co to 525°C, and pressures down to 0.001 mm. Their pyrex still rested directly on top a Gaede mercury vapor pump to avoid the presence of constricting tubing in the vacuu line; the coal sample was distributed in a helical holder around a cold finger type condenser, so that the evaporating surface was about 22 mm from the condensing surfac Vacuum pyrolysis of Pittsburgh Seam bituminous coal yielded semi-solids, yellow to brown in color, as against the liquid coal tars obtained by previous investigators; these semi-solids were considered to be a primary decomposition product which had not existed in the coal prior to distillation.

The vacuum furnace used in the present work was designed to achieve even lower pressures over the sample surface, to decrease the sample-to-condenser distance, and to achieve a more reliable control of temperature than was heretofore possible. The product which condensed at tap water temperature was a solid, reddish-brown, enamel like deposit, not semi-solid or liquid as obtained by previous investigators.

VACUUM PYROLYSIS

Apparatus and Procedure

The distillation apparatus consisted essentially of a vacuum furnace with associated pumps, pressure gauges, and temperature controls. The furnace was de signed to situate the coal sample as near to the condensing surface as possible, and provide an ample, unobstructed passageway for removal of uncondensed gases. Automatic temperature controls gave uniform heating rates, and served to control

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somewhat the rate of gas evolution. An oil diffusion pump as the main vacuum source gave greater pumping capacity than the mercury diffusion pumps and even water aspirators used by previous investigators. The experimental arrangement is illustrated in Figure 1.

Three main sections made up the body of the furnace: a circular base plate which afforded a connection to the vacuum pumps; - a cylindrical steel furnace wall which contained a ground joint through which a thermocouple gauge measured pressures inside the furnace; - and the top assembly, which carried a water-cooled steel condensing surface. The three sections rested lightly one on top of the other, and were sealed by means of lightly greased "O" rings. The assembly is shown in Figures 2 and 3.

The heater was a nichrome spiral embedded in refractory cement, located above the exhaust aperture in the center of the base plate. An aluminum sample pan containing eleven concentric grooves to increase the contact surface to the coal sample, rested on top of the heater and conducted the heat evenly and rapidly to the coal in the grooves. The heater element was completely enclosed by the sample pan, so that all of the heat radiating from its top and sides was intercepted by the pan and thereby made available for heating the coal sample. Downward heat radiation could not be utilized; this heat loss was minimized by a radiation shield.

Extending downward from the base of the furnace, a standard taper steel ground joint was cemented to a 2 1/4 inch diameter pyrex tube by means of a beeswax and rosin seal; the glass tubing narrowed to 1 3/8 inch diameter as it curved into the freezing trap, and continued in this size until it reached the oil diffusion pump. This was an electrically heated three-stage pump similar to Distillation Product Industries Model 6F25W; backed by a Welch mechanical pump, the exhaust rate was 25 liters of gas per second, at 7×10^{-6} mm. A freezing trap located between the furnace and the pumps served to protect the latter from any light condensable fractions which might have distilled over; in addition to its protective function, the trap exerted a considerable pumping action of its own, since removal of condensable materials from the gas phase undoubtedly lowered the total pressure in the system.

The condensing surface (Figure 4) was the bottom of a cylindrical steel well which projected downward from the top plate to a distance of 15 mm above the coal sample. Water inlet and outlet tubes in the top plate allowed the condenser to be cooled by circulating tap water. The pressure in the furnace was measured as close to the coal surface as possible, by a thermocouple gauge which was connected to the spherical joint in the wall of the furnace. This measured pressure probably did not differ greatly from the actual pressure above the coal sample, because of the long mean free paths at these low pressures. The temperature of the sample pan was measured with an iron-constantan thermocouple inserted into the side of the pan, and recorded on the chart of a Brown Electronik recording potentiometer. An automatic heat controller allowed uniform heating of the sample at any desired rate, to any required temperature, and maintenance of this temperature for any length of time.

Pittsburgh Seam bituminous coal was pulverized in a hammer mill and seived to give 40-60 and 60-100 mesh samples. The coal was distributed evenly in the annular grooves of the tared sample pan, which was then positioned on top of the heater. The thermocouple was inserted into the well in the side of the pan, and a grounding wire was attached between the pan and the furnace to minimize stray electrical pickup by the thermocouple leads. The furnace was assembled, and the vacuum pumps started. When the pressure inside the vacuum chamber reached 10^{-4} mm, the heater

was energized; temperatures were recorded continuously on the chart of the Brown instrument, while pressures were written in at intervals of 5-10 minutes. A rapid heat input was required for the first 10 minutes until the temperature reached 270°C; then a slow, controlled heat rise of 2 to 3 degrees per minute until the desired temperature was attained. After 1/2 to 5 hours of distillation at this temperature the furnace was allowed to cool under vacuum, to forestall air oxidation of the contents; when near room temperature, the furnace was vented to the atmosphere or to dry N_2 by means of a stopcock, and the top lifted off.

The distillate appeared as a solid orange-red lacquer which coated the condensing surface with a uniform film. This film was usually removed dry from the condenser by scraping, but occasionally it was dissolved off with a suitable solvent which was afterward removed by evaporation.

Experimental Data

Table 1 summarizes the experimental conditions and presents some of the results of the pyrolyses. Temperatures are given in degrees Centigrade, and times in hours and decimal fractions of an hour. The pyrolysis temperature was the constant temperature at which the sample was thermostatted, while the pyrolysis time was the total time the sample remained within 10°C on either side of this temperature[*].

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[*] The sample pan temperatures were subject to a drift of several degrees on either side of the controlled temperature because the dynamic conditions of heat exchange inside the furnace were not compensated for exactly by the control instrumentation. This drift was usually less than ±5°C, but on occasion it rose to ±10°C.

Figure 5 represents a typical heating curve, and shows the variation of temperature and pressure with time, for a single experiment (No. 16). The pressures are given in ma of current, of the thermocouple pressure gauge; the calibration of this gauge is shown in Figure 6. Ordinarily as the temperature of the coal was raised even slightly above room temperature, an immediate pressure rise was observed, denoting the evolution of small amounts of gases. This gas evolution continued to 240-270°, when the pressure began to drop again, despite the fact that the coal was still being heated and its temperature was still rising: - this was the removal of occluded gases observed by Wheeler (3). It was not observed if the coal had been preheated under vacuum (as it was in experiment 16), since these gases were removed by the preheat. As the temperature continued to increase above 270°C there was no further pressure change until about 350°C, when the pressure again began to rise slowly, continuing to rise as long as the temperature continued to increase. When the temperature became constant, in this experiment at 510°, the gas evolution fell off and the vacuum pumps were able to reduce the pressure after a short time.

Although the temperature at which the pressure inside the furnace began to increase was fairly constant at 380-420°, this was not a valid indication of the temperature at which the coal could be considered as beginning to decompose, because of the efficiency of the vacuum pumps. The temperature of the first observable pressure rise ranged between 310-470° and merely indicated when the rate of gas evolution was approaching the gas moving capacity of the oil diffusion pump, that is 25 liters per second (4).

In order to correlate the experimental data, the sample weight losses were plotted against temperature (Figure 7). This plot was linear, with a fair amount of scatter attributed to the distillation times. Where several experiments showed the same weight loss for different pyrolysis temperatures (e.g. experiments 17, 11, 15), the runs at the lower temperatures were invariably associated with longer distillation times; similarly when several experiments at the same temperature exhibited different weight losses (e.g. experiments 10, 9, 28) then the samples were exposed to elevated temperatures for different lengths of time.

In several experiments the sample was not heated directly to the maximum value near 500°C, but was instead brought to various intermediate temperatures, and the weight loss determined after each heating. Table 2 presents a comparison of these stepwise distillations with direct heating to the final temperature, and shows that there was no appreciable difference in weight loss between samples which were subjected to stepwise pyrolysis and those brought directly to the maximum temperature.

<div align="center">Table 2</div>

<div align="center">Comparison of Stepwise Distillation with Direct Heating to Final Temperature</div>

Expt. No.		Pyrolysis Temperature (°C)	Pyrolysis Time (hrs)	Per Cent (by weight) of Sample Volatilized
Stepwise:	1-1	405	0.67	5.5
	1-2	413	1.05	1.0
	1-3	495	3.83	11.8
	1-4	500	0.92	0
			Total:	18.3
Direct:	12	506	3.25	18.9
Stepwise:	7-1	498	1.25	not measured
	7-2	518	0.67	not measured
			Total:	16.8
Direct:	9	510	1.50	17.3
Stepwise:	20-1	407	1.00	6.6
	20-2	502	0.50	10.2
			Total:	16.8
Direct:	18	500	1.10	17.1

PROPERTIES OF THE SOLID CONDENSATE

Apparatus and Procedure

Molecular Weight: - The average molecular weight of the fragments comprising the solid pyrolysis distillate was determined ebullioscopically by a modified Menzies-Wright method (5). The choice of a suitable solvent for use in the ebulliometer was complicated by the partial solubility of the sample in the solvents commonly employed in this determination; and the average molecular weight of the entire sample was desired, not merely a solvent extract. Therefore a new solvent was required: a pure compound, preferably, which would dissolve the entire sample, be chemically unreactive, have the correct boiling range, and not deviate seriously from Raoult's law.

<div align="center">Table 1</div>

Results of Vacuum Pyrolyses: Yields for Different Times and Temperatures

Expt. No.	Pyrolysis Temperature (°C)	Time at this Temperature (hrs)	Per Cent of Sample Volatilized
2	355	1.17	2.5
24	380	0.75	3.4
27	382	0.62	3.4
25	382	2.17	3.7
26	380	1.75	3.7
23	380	0.58	3.8
30	392	1.00	3.8
22	376	1.83	4.0
1-1	405	0.67	5.5
3	405	1.30	6.0
20-1	407	1.00	6.6
21	400	4.55	7.1
4	456	2.33	12.1
29	458	2.20	14.1
13	455	3.90	15.7
28	510	1.50	16.6
18	500	1.10	17.1
9	510	1.50	17.3
12	506	3.25	18.9
16	512	4.85	19.8
11	530	2.83	20.6
17	515	4.00	20.6
15	535	2.55	20.9
14	520	2.83	21.5
10	510	3.33	22.6

A better estimate of the decomposition temperature came from the first appearance of the solid distillate on the condensing surface. This was found to occur at 355°, several degrees lower than the temperature at which the pressure began to rise in the furnace. No solid distillate was ever observed at temperatures as low as 270°C.

The weight loss of the sample pan after an experiment represented the sum of the volatiles distilled out of the coal, plus degradation products liberated as a result of the thermal treatment. This weight loss ranged from 2.5 per cent to nearly 23.0 per cent depending upon experimental conditions, - in good agreement with the 28 per cent weight loss reported by Juettner and Howard (2). The quantity of solid distillate actually recovered was 40 per cent to 50 per cent of the total weight loss. Except for small mechanical losses, the bulk of the unrecovered pyrolysis products were made up of substances which were volatile at tap water temperature. These included non-condensable gases such as carbon monoxide, carbon dioxide, and methane, plus moisture and traces of liquors and light oils; the latter were frozen out to prevent them from polluting the vacuum pumps. Since the interest lay primarily in the condensate which was solid at tap water temperature, and not in the gaseous or liquid products, no attempts were made to recover these or to calculate a material balance. Yields of solid condensate were not determined because the deposits on the salt plates and the cement holding these plates could not be measured accurately.

No suitable pure compound was found; however mixtures of methanol and benzene dissolved the sample completely (although neither alone was able to do so), and appeared otherwise desirable, so that the methanol-benzene azeotrope was chosen as the solvent for the molecular weight determinations. The azeotrope was prepared as needed by distillation through a 2 ft adiabatic column packed with helices. Removal of water from the methanol and benzene was not necessary since there is no water-methanol-benzene azeotrope; any water which may have been present was left in the pot.

The ebulliometer was calibrated by adding successive portions of known solutes (diphenyl, Eastman 721, and diphenyl phthalate, Eastman 708, used without further purification) to a 25 ml aliquot of boiling solvent, and plotting the boiling point elevation against the number of moles of solute added. The molecular weight of unknown samples could then be calculated from the boiling point elevation for measured sample weights.

Absorption Spectra: - Absorption spectra of liquid derivatives from coal such as solvent extracts, hydrogenation products, and distilled tars are easily obtained; but the solid condensates were only partially soluble in nonpolar solvents (e.g. -carbon tetrachloride, carbon disulfide, chloroform) and so the spectra of solutions in the solvents were not representative of the complete sample. Absorption spectra obtained directly from the solid sample were preferable, but no completely satisfactory technique was known; Nujol mulls (6), thin sections (7,8) and KBr pelleting (9) all had disadvantages. In a new technique, advantage was taken of the vapor phase condensation by which the solid distillate was formed. A rock salt or a KBr plate was mounted directly above the coal sample in the furnace, and the vapor allowed to condense directly upon it (10); the coated plates were then inserted in the spectrometer, and spectra were determined directly from the solid samples. Uniform coatings were obtained, the samples were easily handled, and the opportunities for chemical changes to take place as a result of handling the sample in air, treatment with solvents, grinding with KBr, etc. were minimized.

NaCl plates were cemented directly to the condenser surface using rubber cement (Figure 4). These plates were removed from the furnace immediately after each experiment and placed in a desiccator until they could be examined. In some cases where the pyrolyses were conducted at low temperatures (355-380°C) the plates were too thinly coated to yield satisfactory spectra, and they were allowed to remain in the furnace throughout several pyrolyses to allow a heavier coating to be built up. On occasion a knife edge was mounted over the NaCl plate to cast a shadow and provide a coating whose thickness varied continuously along one dimension of the plate. By moving this plate in front of the spectrometer aperture it was subsequently possible to locate the optimum sample thickness, and obtain the best spectra.

Infrared spectra were obtained with a Perkin Elmer Model 21 double beam spectrometer, using a polished NaCl plate in the reference beam. Ultraviolet spectra were obtained with a Cary Model 11 instrument, using air as the reference material instead of the polished NaCl plate.

Density: - The density of the solid condensate was determined by a sink-or-float method in brine. The samples as scraped from the condensing surface consisted originally of irregularly shaped particles containing entrapped air which caused them to float even in pure water. It was necessary to heat the sample in water to

its softening point, to liberate this entrapped air; after cooling, it was transferred to the thermostatted container containing the brine solution.

Saturated brine solutions were prepared by adding NaCl (Baker and Adamson reagent grade, used without further purification) to boiling distilled water and allowing the solutions to cool; a quantity of distilled water was boiled for several minutes to remove dissolved air, and this too was allowed to cool. Brines of varying concentrations were prepared by mixing these two solutions, rather than by adding NaCl crystals directly to the system containing the sample.

Equilibrium was approached from both directions: saturated NaCl solutions containing the entire sample at the surface were diluted by dropwise addition of the air-free distilled water until the particles sank; and dilute NaCl solutions containing the sample at the bottom were concentrated by dropwise addition of saturated NaCl solution until the particles floated. At equilibrium most of the sample hung suspended in the body of the solution, with apparently equal numbers of particles moving upward and downward. The density of the solution at this point was taken as the density of the sample.

Refractive Index: - The refractive index was measured with an Abbe refractometer; however, considerable interference was experienced from the solid form and the intense color of the sample. Transmission of light through pyridine solutions or through the melted sample on a heated stage was low. However, successful measurements were made by troweling a thick slurry of the sample in methanol-benzene directly to the underside of the top prism and allowing it to set to a tacky, semi-solid mound, eventually drying to a solid mass. Since the slurry originally wetted the glass, this mound was in close contact with the prism. Refractive index measurements were made by reflected sodium D light at 25°C.

Softening Temperatures: - A few particles of sample were inserted between cover glasses on the electrically heated stage of a low power (60x) microscope, which was illuminated simultaneously from above and below to provide top illumination of the specimen against a white field. Melting was observed as the wetting of the top cover glass at points of contact between particles and glass, the rounding off of rough edges of the smallest particles, and the disappearance of scratches and gouges from the fracture surfaces of the larger particles. An iron-constantan thermocouple was used to measure temperatures.

Solubility: - Several particles of the sample were placed in a test tube and 5 ml of solvent were added, at room temperature. Complete disappearance of the solid phase was taken as complete solubility; heavy coloration of the solvent with solid phase remaining was taken as partial solubility; but very slight coloration of the solvent was ignored if the bulk of the solid remained, and the sample considered insoluble.

Experimental Data

Appearance: - The solid pyrolysis distillate coated the condensing surface as a transparent lacquer, initially yellow-orange in color, but rapidly turning red-brown and then black, in air and light. Under the microscope the black substance was observed to be still red-brown to transmitted light. The solid was amorphous and broke with a conchoidal fracture. No crystal structure was visible, and all attempts to induce crystallization proved unsuccessful.

Softening Temperatures: - No sharp, definite melting point was observed. When freshly prepared, the condensates softened as low as 45°C; however, air oxidation of thin films on glass or NaCl plates, or extended exposure to elevated temperatures raised the softening temperatures to as high as 180°C.

Chemical Analysis: - Proximate and ultimate analyses for the same Pittsburgh Seam bituminous coal used in these experiments have been reported by R. A. Glenn (11). Table 3 gives carbon and hydrogen analyses for the solid condensate, the residual char, and the parent coal substance.

Table 3

Carbon - Hydrogen Analysis of Pittsburgh Seam Coal, Solid Condensate, and Char[1]

	Original Coal[2] (%)	Solid Condensate (%)	Solid Char (%)
Carbon:	78.48	84.99	76.41
Hydrogen:	5.60	7.48	4.01
Residue on combustion:	3.84	0.47	11.05
Atomic C/H ratio:	1.12	0.95	1.82

[1] Huffman Laboratories, Wheatridge, Colorado.

[2] As received, not on an ash and moisture free basis.

Molecular Weight: - Methanol and benzene form a minimum boiling azeotrope at the composition 39.6 per cent methanol and 60.4 per cent benzene, which boils at 58.3°C, at 760 mm (12). The boiling point of the azeotrope varied between 57.3° and 57.6° due to daily barometric fluctuations between 735.5 and 742.0 mm, averaging 57.55°C at 739 mm. When corrected to 760 mm by Young's equation (13):

$$\Delta t = (760 - p)\,(T)\,(C) \tag{1}$$

where Δt = temperature to be <u>added</u> to correct the boiling temperature to 760 mm,
    p = observed pressure, 739 mm.
    T = measured temperature, 330.71°K
    C = a constant = 1.1×10^{-4} for methanol-benzene

the corrected boiling point was 58.3°C, in agreement with the literature value.

Figure 8 presents the ebulliometer calibration, a plot of boiling point elevations against moles of solute added. The curve was constrained to pass through the origin, since zero solute gave zero boiling point elevation; and the best straight line as calculated by a least squares treatment was drawn through the data points. The slope of this curve was 553.13 and the average deviation from this value was less than 3 per cent. This linear calibration plot indicated that methanol-benzene was a suitable solvent for use in the ebulliometer, and inferred that the azeotrope obeyed Raoult's law, or at least deviated from it by only a small

amount; also that association, dissociation, or chemical reactions between solute and solvent were at a minimum, since these effects would have caused the data points to deviate from a straight line.

The ebulliometer equation was: $\Delta t = 553.13 \ (W/M)$ (2)

where: Δt = boiling point elevation (cm water)
$\quad\quad$ W = weight of solute (gm)
$\quad\quad$ M = molecular weight of solute (gm/mole)

The molecular weights of the unknown samples were then determined by:

$$M = 553.13 \ (W/\Delta t) \tag{3}$$
$$M = \frac{553.13}{A} \tag{4}$$

where A = slope of plot of Δt against W, for the unknown solute.

Table 4 gives the results of molecular weight determinations on several solid pyrolysis condensates:

<div align="center">Table 4</div>

Solute	Molecular Weight
Solid condensate, expt. 4	266
Solid condensate, expt. 2	279
Solid condensate, expt. 7	270
Average, rounded off to 2 significant figures	270

Absorption Spectra: - Figure 9 is representative of the infrared spectra obtained, and shows the absorption spectrum of the solid condensate of a typical pyrolysis. Comparison of the spectra of the condensates with the original coal was desired; but only the spectra of the Anthraxylon constituent of Pittsburgh Seam coal was available (8), and not spectra of the whole coal. These published spectra were considered appropriate, since Pittsburgh Seam coal is approximately 85 per cent anthraxylon, and this petrographic constituent is probably the most susceptible to pyrolysis and distillation. Friedel has suggested that infrared studies of coal be conducted preferably on the anthraxylon constituent and not on the whole coal, because the latter offers considerable interference from minerals (8). The infrared spectrum for a thin section of anthraxylon is shown in Figure 10.*

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* Figure 10 and the information in column 2 of Table 5 were not obtained from reference 8, but from the original spectra, loaned by Dr. Fridel.

It is immediately apparent that the infrared absorption spectrum of the solid condensate is essentially identical with the spectrum of the anthraxylon thin section. The shapes of the absorption bands and the shoulders on these bands are remarkably similar; and the locations of the bands and shoulders (Table 5) are identical within the limits of experimental accuracy. The relative intensities of adjacent bands are the same in both spectra, with a few small, but possibly significant differences. The band at 3.0 µ is somewhat less intense in the solid

condensate than in the original coal, possibly as a result of some loss of OH
or NH in the course of the pyrolysis; however, this 3.0 μ band was found to vary
considerably between samples, and aging of the samples produced changes too.
The slight differences in the relative intensities of the 7.95 μ and 13.38 μ
bands, between the two spectra, resemble shifts observed in the spectra of
mixtures, when there is a change in the proportions, but not in the identity of
the components. When the pyrolyses were conducted at low temperatures (about
380°C), a slight sharpening of the absorption bands was noted: more important,
the very strong band at 6.21 μ was split into 2 bands having maxima at 6.07 μ
and 6.20 μ, while the 3.0 μ band was shifted to 3.17 μ. The general appearance
of the spectra remained unchanged.

Table 5

Absorption Maxima of Infrared Spectra (10)

Pittsburgh Seam Coal Vacuum Pyrolysis Distillate Film Approx. 0.02 mm Thick on NaCl Plate	Pittsburgh Seam Coal Anthraxylon (0.020 mm Petrographic Section)	Description
μ	μ	
2.34 ± 0.02	2.32	weak band
2.84	2.86	weak shoulder
3.02	3.00	band
3.31	3.30	strong shoulder
3.44	3.43	band
3.49	3.49	shoulder
5.26	5.25	broad dip
6.21	6.20	strongest band in spectrum
6.48	6.47	shoulder near hump
6.77	6.75	shoulder
6.92	6.88	band
7.28	7.27	band
7.92	7.92	broad dip
9.70	9.68	band
9.96	9.95	faint shoulder
10.60	10.55	shallow band
11.60	11.60	broad band
12.32	12.25	broad band
13.36 ± 0.04	13.30	broad band

Figure 11 shows the ultraviolet spectrum for a typical solid condensate, be-
tween 2100 and 4000 A°. Initially the only ultraviolet spectra which could be
observed were either zero absorption (sample too thin) or total extinction
(sample too thick). When a continuous variation of sample thickness was achieved
by having a knife edge cast a "shadow" on the NaCl plate during pyrolysis, it was pos-
sible to obtain the ultraviolet spectra of the solid distillates. These spectra
show maxima at 2250 A° and 2600 A° in addition to a slight hump in the curve at
2975 A°. Since ultraviolet spectra have not been reported for coal in this range of
wavelengths, due to the excessive dispersion of the thin sections, Nujol mulls, and
KBr pellets, no comparison with the original coal could be made. However, the
ultraviolet spectra were found to resemble the spectra of coal extracts. Barclay
and Layton (14) obtained similar spectra from solvent extraction of bituminous
coals, with absorption maxima at 2300 A° and 2600 A°.

Molar Refraction: - Molar refractions were calculated from the Lorentz-Lorenz equation (15,16), using the measured values of the physical properties, Table 6.

$$[R]_D = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$$

(5)

Table 6

Physical Properties of the Solid Condensate

Molecular weight: $M = 270$

Density: $d_{25°} = 1.171$ g/ml

Refractive index: $n_D^{25} = 1.668$

Molar refraction: (calculated) $[R]_D = 85.9$ cc

Solubility: - Table 7 presents some coarse determinations of solubility in various organic and inorganic solvents.

Table 7

Solubility of Solid Condensate in Various Solvents

Insoluble	Partly Soluble	Soluble
Water	benzene	H_2SO_4, concd.
NaOH, concd. and dil.	methanol	Phenol above its melting point
HCl, concd. and dil.	dioxane	Other organic bases such as pyridine,
H_3PO_4, syrupy	chlorobenzene	quinoline, aniline, dimethylformamid
Acetic acid	α-bromonapthalene	etc.
Acetic anhydride	carbon tetrachloride	Various phenol-water solutions
	chloroform	Aromatic hydrocarbons as napthalene,
	carbon disulfide	anthracene, phenanthrene, above thei melting points.

Vapor Sorption: - The sorption of β-methoxyethylamine vapor on the solid condensate and the residual char was compared with sorption on coal, by the method of R. Trammel (17). Table 8 shows that the solid condensates sorbed irreversibly about 4 times the weight of amine as the char and the coal. The values for the latter were essentially the same, indicating that the coal was not extensively degraded in its transition to char.

Table 8

Sorption of β-Methoxyethylamine Vapor on Solid Condensate,
Residual Char, and Parent Coal, at 35°C.

	Solid Condensate No. 18	Solid Condensate No. 29	Residual Char No. 29	Anthraxylon (-100 mesh)
Sample before drying:	0.1766 g	0.1855 g	0.1768 g	0.2020 g
Sample after drying:	0.1766	0.1852	0.1768	0.2018
Sample after evacuation:	0.1766	0.1849	0.1768	0.1999
Weight amine sorbed (mg):	15.12 mg	15.38 mg	4.17 mg	4.28 mg
W_p (mg/grams sample):	85.61 mg/g	83.19 mg/g	23.60 mg/g	21.39 mg/g

Discussion

Bituminous coal ordinarily softens and swells up under the action of heat at atmospheric pressure, and the particles of coal fuse together in the preliminary stages of the coking process. After vacuum pyrolysis however, the residual char continues to resemble strongly the original coal sample; there is no caking, no agglomeration, and practically no swelling of the particles. The similarity of the vacuum pyrolysis char to the parent coal substance is also pointed up by their similar behavior to sorption of amines, and indicates again that the coal has not been extensively degraded in forming the char.

Infrared spectral analysis discloses that the solid condensate resembles the original coal in a striking manner, so that it has probably not been far degraded from its original form in the coal. Apparently some portion of the coal responsible for the characteristic spectrum has distilled over unchanged. Although there are similarities between Figure 9 and the spectra of other coal products, such as asphaltenes from hydrogenation of Pittsburgh Seam coal (8) and benzene extracts from this same coal (18), it is evident that the solid condensates resemble the parent coal much more than they resemble other coal derivatives.

Vacuum pyrolysis of coal appears, then, to constitute a gentle degradation which gives rise to little secondary cracking; this is further substantiated by the neutral character of the solid condensate (solubility class N_2) and the absence of appreciable quantities of liquid oily condensates. Since the solid condensates may be considered to be primary decomposition products, then a study of their physical properties should give an insight into the chemical composition of coal.

Coal distillates are predominantly hydrocarbons, whose structure may be made up of combinations of the various groups:

1. Paraffins (saturated aliphatic groups)
2. Napthenes (cyclic paraffins)
3. Aromatic rings
4. Aliphatic groups having isolated olefinic linkages

The ready solubility of the solid condensate in cold concd. H_2SO_4 rules out fully saturated hydrocarbons, and suggests that fully aromatic hydrocarbons without side chains are probably not present. Poll (19) has shown that olefins are absent from distilled bitumens, and Friedel (8) has found no evidence for unconjugated olefinic linkages in coals and coal distillates. Friedel feels that long paraffinic side chains and condensed polynuclear aromatic ring structures are also absent from coal.

Chemical analysis of the solid condensate has determined that the atomic C/H ratio is 0.95; since this ratio increases with increasing numbers of fused aromatic rings (benzene = 1.0, napthalene = 1.25, etc.) it is clear that the sample is not fully aromatic. Since the ultraviolet spectra (Figure 11) do not exhibit the vibrational fine structure characteristic of condensed polynuclear aromatic ring structures, it is fairly certain that the solid condensate contains few, if any, condensed aromatic rings.

One possibility has not yet been considered: namely, isolated aromatic rings fused into hydroaromatic configurations, and containing aliphatic side chains limited in size to ethyl groups.

The relatively high refractive index (considering that the sample is not crystalline, but rather a supercooled liquid), and the intense red-brown coloration are indications of a complex resonating structure which might ordinarily be explained by conjugation in a highly aromatic molecule. Any suggested molecular configuration for the solid condensate must satisfy the opposing requirements of the spectra on the one hand, and the refractive index on the other.

The molecular weight of 270 limits the size of the molecule, and the C/H ratio defines the degree of unsaturation; taking into consideration the improbable structures outlined above, it is possible to write down a number of molecular models. For example:
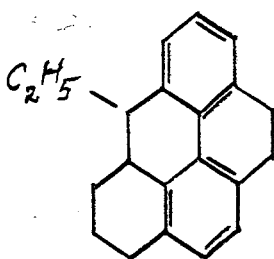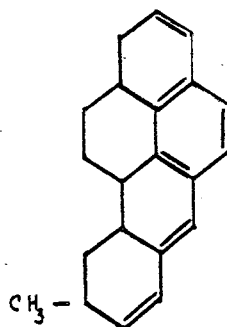
(A)   (B)

Empirical formula:	$C_{21}H_{22}$
Molecular weight:	274
C/H ratio:	0.95

The proposed molecular models must also be in agreement with the measured molar refraction of 85.9 cc. Eisenlohr (20) has tabulated Refraction Equivalents of various atoms and structural groups:

Table 9

Refraction Equivalents for Sodium - D line

Carbon	2.418
Hydrogen	1.100
Double bond	1.733

By this tabulation, both structures (A) and (B) having 21 carbon atoms, 22 hydrogen atoms, and 6 double bonds, have the calculated molar refraction: $[R] = 85.4$ cc. Calculation of the molar refraction using the bond refractions of Smyth (21) and Fajans (22) instead of the refraction equivalents, gives the same value, namely $[R]_D = 85.4$ cc.

If the molecule is assumed to be spherical (perhaps not too justifiably), then an estimate of the molecular radius (r) may be made from a part of the Lorentz-Lorenz relation:

$$[R] = (4/3) \pi N r^3 \tag{5}$$

Substituting the measured value of molar refraction and Avogadro's number gives: r = 3.24 A°, or a molecular diameter of 6.48 A°. This may be compared with Hirsch's determination (23) that the average diameter of the condensed aromatic layers in _coal_ are 7 to 8 A°, corresponding to 4 or 5 condensed rings.

It is too early to decide between structures (A) and (B) or similar models, since it is not even certain that the solid condensate consists of a single sub-stance. It is more likely a complex mixture containing many isomers with similar configurations. Therefore, while individual pure compounds might have absorption spectra showing more fine structure than Figures 9 and 10, it is possible that in mixtures so complex as those derived from coal, only the most outstanding features can persist and be recognized as absorption bands in the spectra. The lack of fine structure in the ultraviolet spectra may similarly be due not only to the smoothing action of aliphatic side chains and hydrogen substitution for conjugated aromatic structures, but also to the possibility that the sample is a mixture.

This presentation is intended as an introduction to some of the properties of the solid which condenses at tap water temperature, during vacuum pyrolysis of bituminous coal. Further characterization of this substance must await the results of additional investigations at the Coal Research Laboratory.

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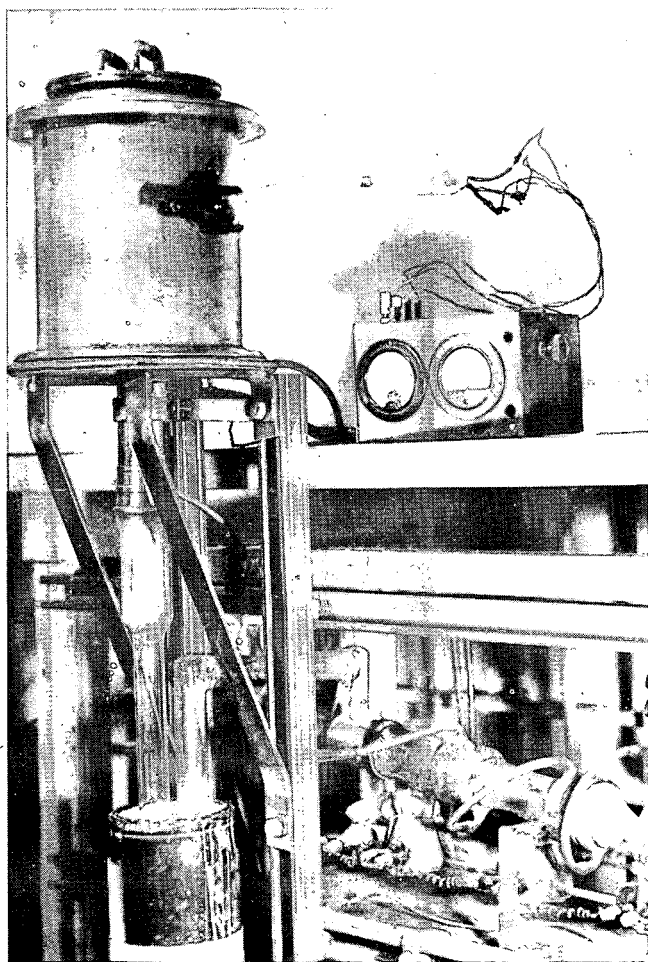23. Hirsch, P. B., Proc. Roy. Soc. (London), A-226, 143 (1954).

Fig. 1 -- General View of Vacuum Pyrolysis Apparatus: Furnace,
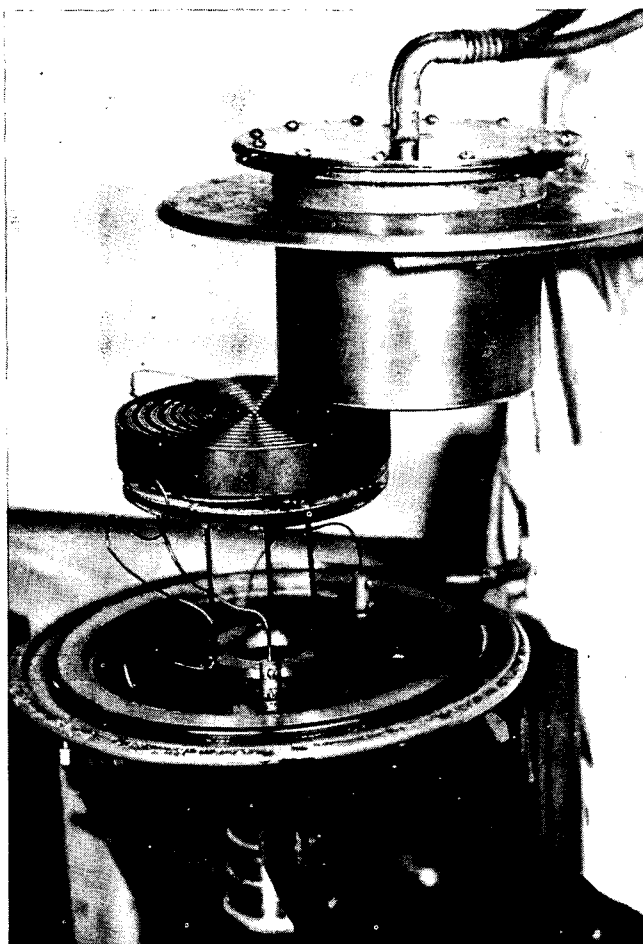Cold Trap, Oil Diffusion Pump, and
Thermocouple Pressure Gauge

Fig. 2 -- Interior of Vacuum Furnace (Condenser offset to
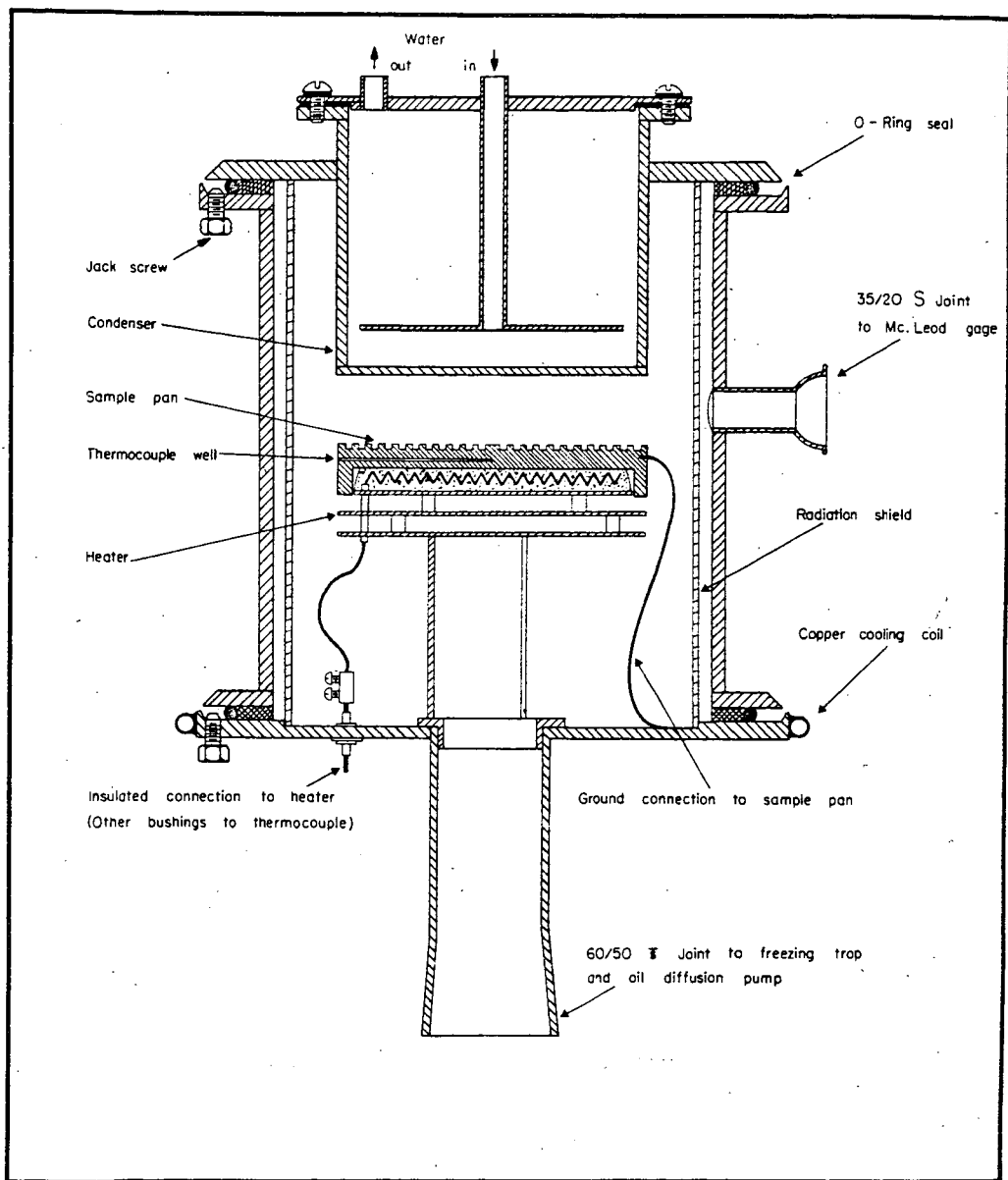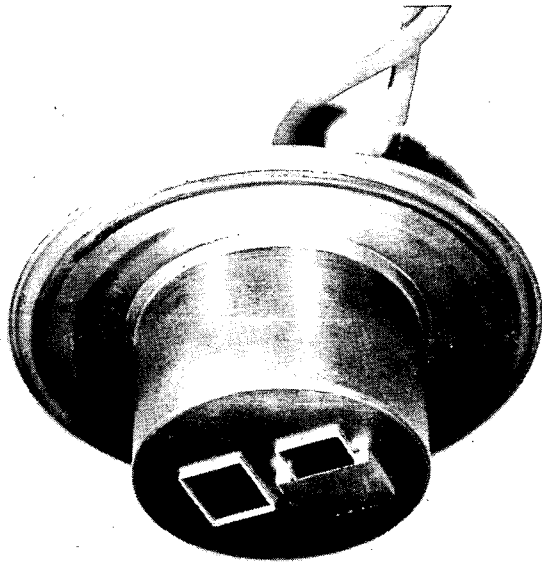show sample pan more clearly).

Water
out   in

O - Ring seal

Jack screw

Condenser

Sample pan

Thermocouple well

Heater

35/20 S Joint
to Mc. Leod gage

Radiation shield

Copper cooling coil

Insulated connection to heater
(Other bushings to thermocouple)

Ground connection to sample pan

60/50 T Joint to freezing trap
and oil diffusion pump

FIG. 3 -- VACUUM FURNACE

Fig. 4 -- Assembly of Salt Plates on Condenser Surface
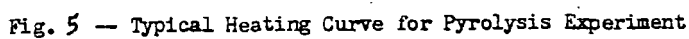
Fig. 5 — Typical Heating Curve for Pyrolysis Experiment
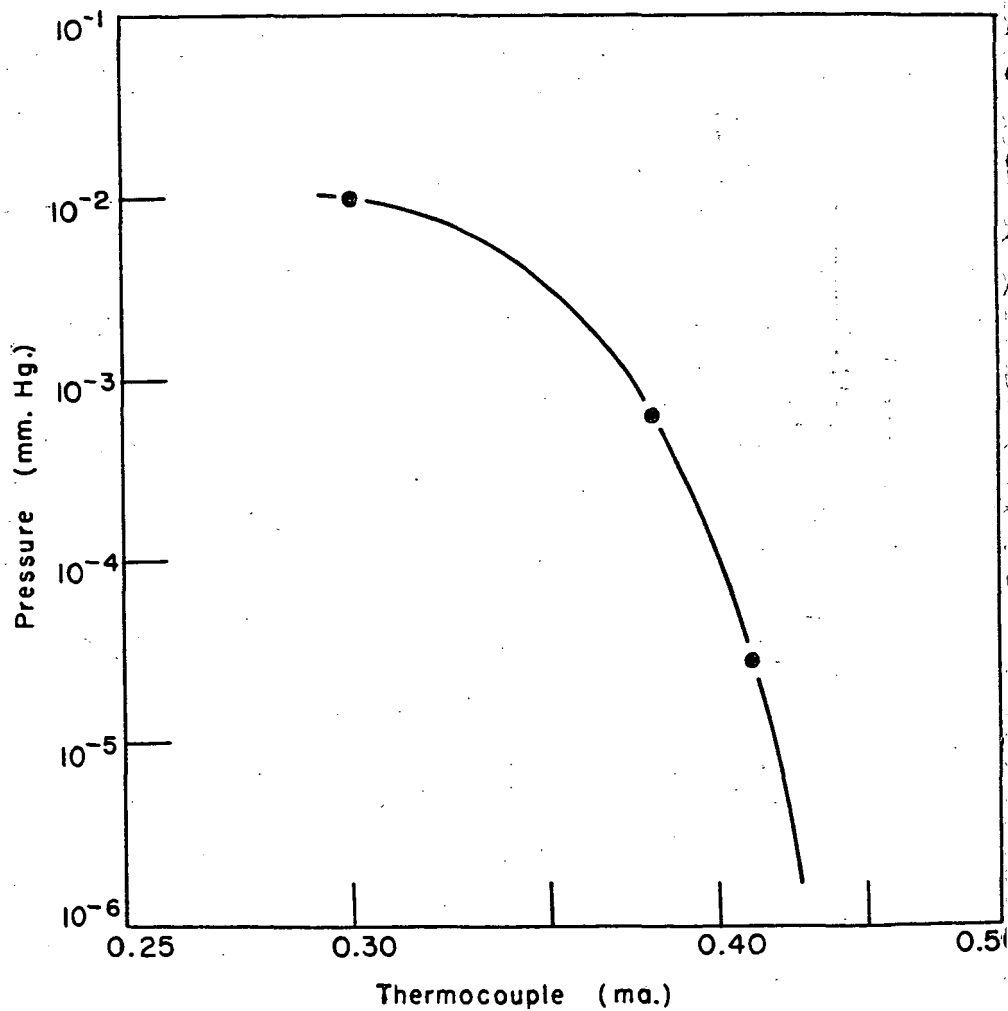
Fig. 6 -- Calibration of Thermocouple Pressure Gauge
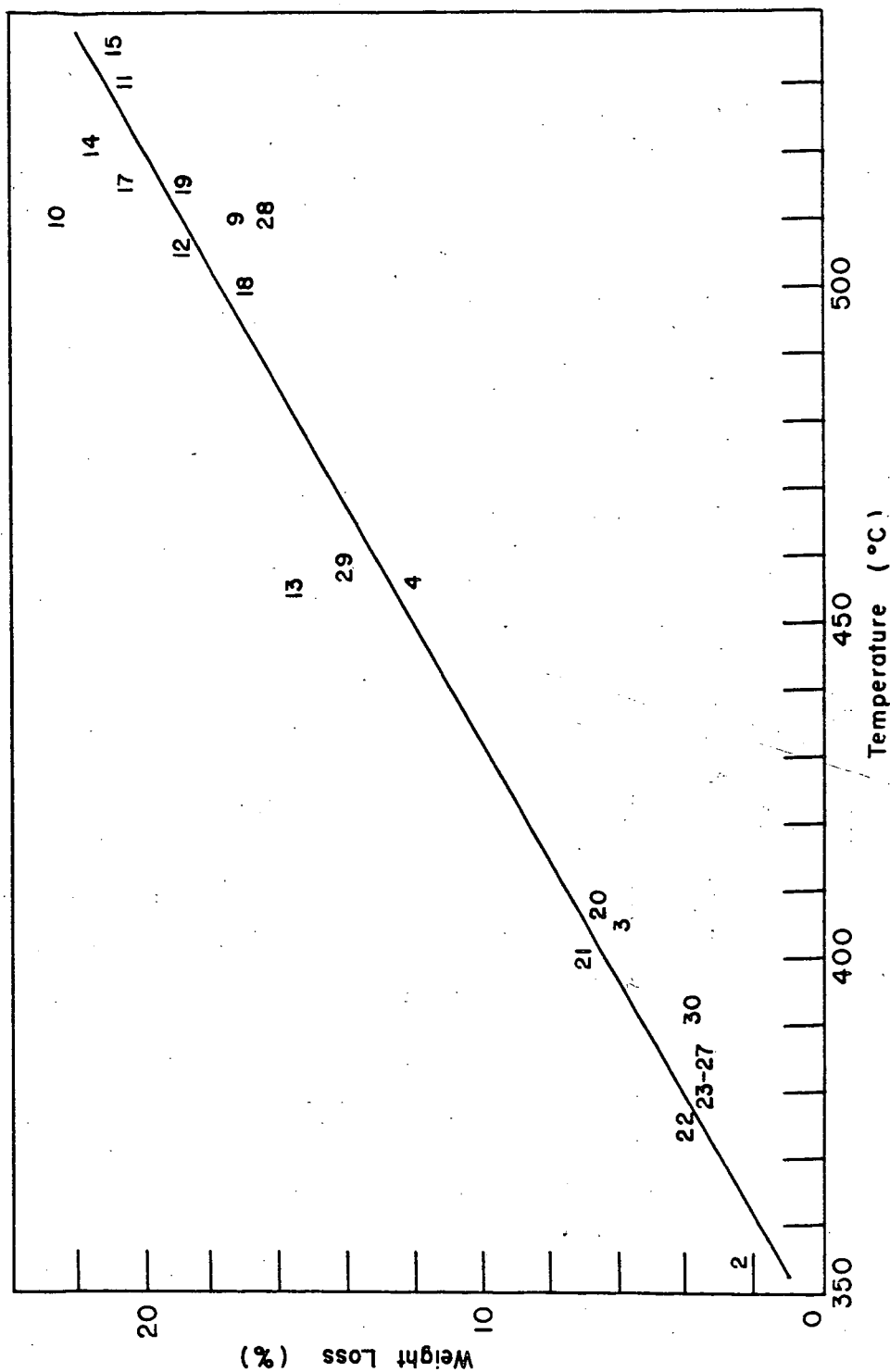
Fig. 7 -- Relation of Sample Weight Loss to Pyrolysis Temperatures
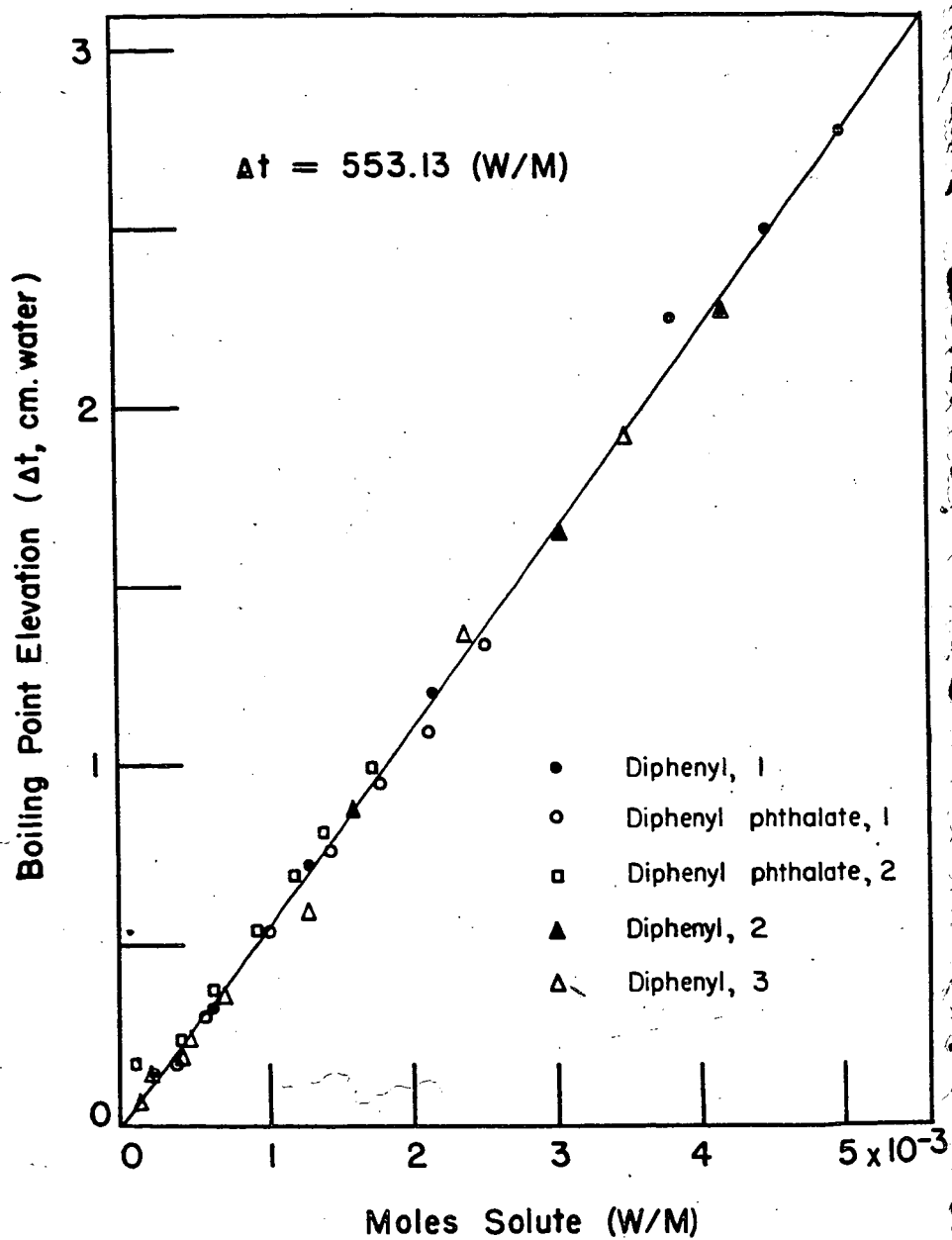
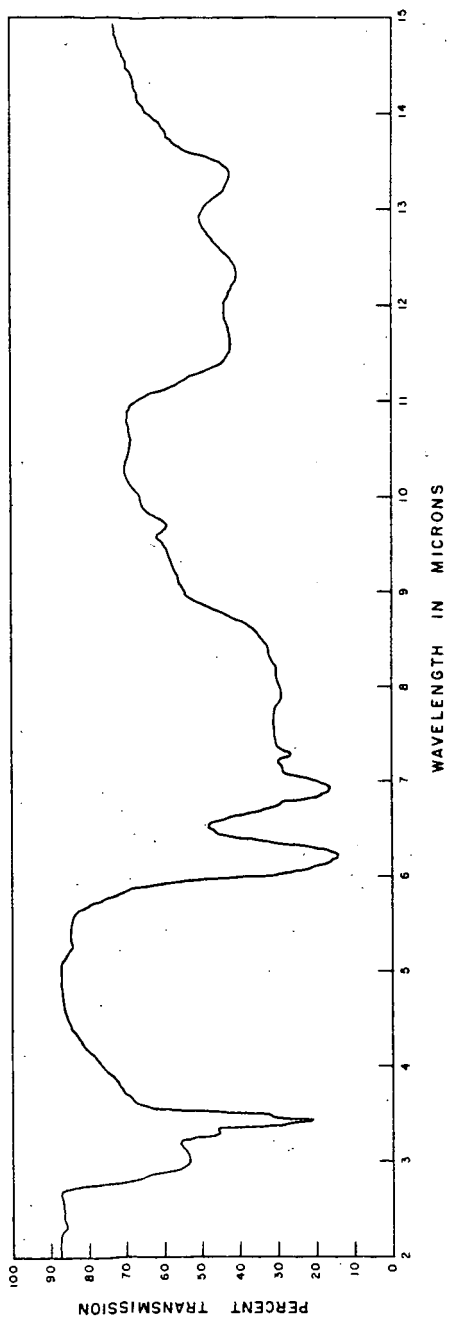Fig. 8 - Calibration of Ebulliometer and Methanol-Benzene Solvent

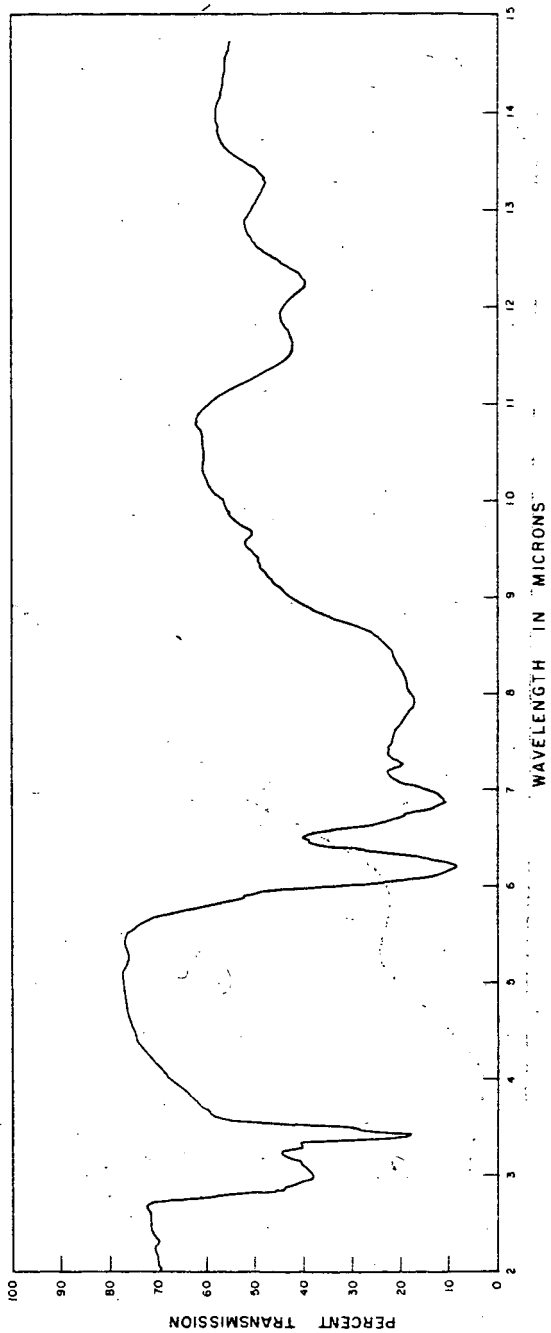Fig. 9 -- Typical Infrared Spectrum of Solid Condensate

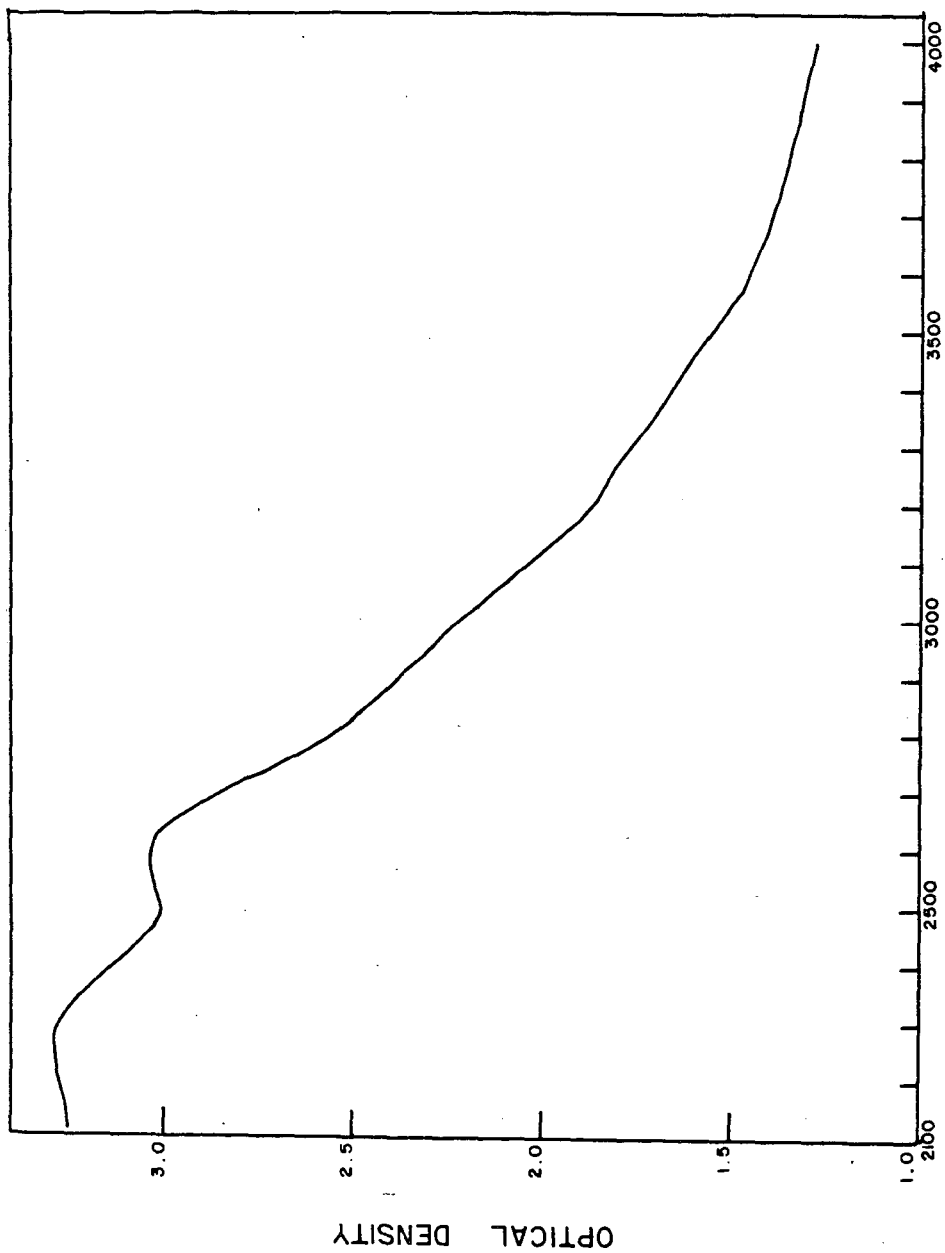Fig. 10 -- Infrared Spectrum of a Thin Section of Anthraxylon

WAVELENGTH IN ANGSTROMS

Fig. 11 -- Typical Ultraviolet Spectrum of Solid Condensate